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A rapid technique for the direct metallization of PDMS substrates for flexible and stretchable electronics applications

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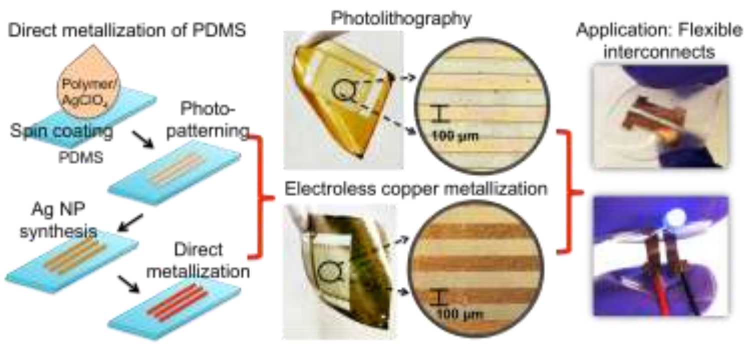
Highlights

- Crack-free deposition of electroless copper over the elastomeric surface;
- Strong metal-to-PDMS surface adhesion; copper film remains conductive whilst it undergoes bending and stretching deformations;
- Copper-plated PDMS have high flexibility (up to 180°).

Abstract

Direct metallization of polydimethylsiloxane (PDMS) is a challenge due to the difficulties forming a crack-free photoresist and metal features on its surface, by sputtering processes. Frequently, additional adhesion layers, rigid substrates, multi-steps (lift off and etching) and expensive metal sputtering techniques are required, to achieve crack-free photoresist and metal patterns on PDMS. This work presents a novel and rapid technique for successful direct metallization of PDMS substrates by a reliable photolithography procedure and electroless copper plating methods, which additionally does not require expensive vacuum processing or multiple metallization steps. Electroless copper layer has a strong adhesion to PDMS substrate with a high conductivity of $(3.6 \pm 0.7) \times 10^7$ S/m, which is close to the bulk copper (5.9×10^7 S/m). The copper-plated PDMS displays mechanical and electrical stability whilst undergoing stretching deformations up to 10% due to applied strain. A functional electronic circuit was fabricated as a demonstration of the copper-plated PDMS bending stability.

Graphical abstract



Keywords: copper-plated PDMS, direct metallization, electroless plating, flexible electronics

1. Introduction

Stretchable and flexible electronics have recently received a great interest in multiple applications such as wearable electronics, soft robotics, displays and bioelectronics **{** ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1021/acs.chemmater.7b00181", "ISBN" : "0897-4756", "ISSN" : "15205002", "abstract" : "The fabrication of stretchable electronic devices is presently rather challenging on account of both the limited number of materials showing the desired combination of mechanical and electrical properties and the lack of techniques to process and pattern them. Here we report on a fast and reliable transfer patterning process to fabricate high-resolution metal microelectrodes on polydimethylsiloxane (PDMS) by using ultrathin Parylene films (2 \u03bcm thick). By combining transfer patterning of metal electrodes with orthogonal patterning of the conducting polymer poly(3,4-ethyl-enedioxythiophene) doped with polystyrenesulfonate (PEDOT:PSS) on a prestretched PDMS substrate and a biocompatible \" cut and paste \" hydrogel, we demonstrated a fully stretchable organic electrochemical transistor, relevant for wearable electronics, biosensors, and surface electrodes to monitor body conditions.", "author" : [{ "dropping-particle" : "", "family" : "Zhang", "given" : "Shiming", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Hubis", "given" : "Elizabeth", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Tomasello", "given" : "Gaia", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Soliveri", "given" : "Guido", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Kumar", "given" : "Prajwal", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Cicoira", "given" : "Fabio", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Chemistry of Materials", "id" : "ITEM-1", "issue" : "7", "issued" : { "date-parts" : [["2017"]] }, "page" : "3126-3132", "title" : "Patterning of Stretchable Organic Electrochemical Transistors", "type" : "article-journal", "volume" : "29" }, "uris" : ["http://www.mendeley.com/documents/?uuid=18206df1-875c-4905-a356-f42358a9a55e"] }], "mendeley" : { "formattedCitation" : "[1]", "plainTextFormattedCitation" : "[1]", "previouslyFormattedCitation" : "[1]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }**}**. The increasing demand for flexible microelectronic systems requires the development of flexible circuits with interconnections that can withstand mechanical stresses under high strains **{** ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1038/s41598-018-27798-z", "ISSN" : "20452322", "abstract" : "Here, we study cracking of nanometre and sub-nanometre-thick metal lines\n(titanium, nickel, chromium, and gold) evaporated onto commercial\npolydimethylsiloxane (PDMS) substrates. Mechanical and electromechanical\ntesting reveals potentially technologically useful effects by harnessing\ncracking. When the thin film metal lines are subjected to uniaxial\nlongitudinal stretching, strain-induced cracks develop in the film. The\nregularity of the cracking is seen to depend on the applied longitudinal\nstrain and film thickness-the findings suggest ordering and the\npossibility of creating metal mesas on flexible substrates without the\nnecessity of lithography and etching. When the metal lines are aligned\ntransversally to the direction of the applied strain, a Poisson\neffect-induced electrical `self-healing' can be observed in the films.\nThe Poisson effect causes process-induced cracks to short circuit,\nresulting in the lines being electrically conducting up to very high\nstrains (similar to 40%). Finally, cracking results in the observation\nof an enhanced transversal gauge factor which is similar to 50 times\nlarger than the geometric gauge factor for continuous metal\nfilms-suggesting the possibility of high-sensitivity thin-film metal\nstrain gauge flexible technology working up to high strains.", "author" : [{ "dropping-particle" : "", "family" : "Ba\u00ebtens", "given" : "Tiffany", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Pallecchi", "given" : "Emiliano", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Thomy", "given" : "Vincent", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Arscott", "given" : "Steve", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Scientific Reports", "id" : "ITEM-1", "issue" : "1", "issued" : { "date-parts" : [["2018"]] }, "page" : "1-17", "title" : "Cracking effects in squashable and stretchable thin metal films on PDMS for flexible microsystems and electronics", "type" : "article-journal", "volume" : "8" }, "uris" : ["http://www.mendeley.com/documents/?uuid=f987dc29-fc06-4cf0-a067-af3c5e5207a6"] }], "mendeley" : { "formattedCitation" : "[2]", "plainTextFormattedCitation" : "[2]", "previouslyFormattedCitation" : "[2]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" } **}** . Various nanocomposite materials and elastic polymers are investigated as soft substrates for fabrication of flexible electronic devices with stretchable interconnections linking electronic parts.

PDMS elastomer is an excellent candidate for flexible and elastic electronics due to its stretchable and bending characteristics **{**ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1038/micronano.2016.43", "ISSN" : "2055-7434", "abstract" : "There are now numerous emerging flexible and wearable sensing technologies that can perform a myriad of physical and physiological measurements. Rapid advances in developing and implementing such sensors in the last several years have demonstrated the growing significance and potential utility of this unique class of sensing platforms. Applications include wearable consumer electronics, soft robotics, medical prosthetics, electronic skin, and health monitoring. In this review, we provide a state-of- the-art overview of the emerging flexible and wearable sensing platforms for healthcare and biomedical applications. We first introduce the selection of flexible and stretchable materials and the fabrication of sensors based on these materials. We then compare the different solid-state and liquid-state physical sensing platforms and examine the mechanical deformation-based working mechanisms of these sensors. We also highlight some of the exciting applications of flexible and wearable physical sensors in emerging healthcare and biomedical applications, in particular for artificial electronic skins, physiological health monitoring and assessment, and therapeutic and drug delivery. Finally, we conclude this review by offering some insight into the challenges and opportunities facing this field", "author" : [{ "dropping-particle" : "", "family" : "Kenry", "given" : "", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Yeo", "given" : "Joo Chuan", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Lim", "given" : "Chwee Teck", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Microsystems & Nanoengineering", "id" : "ITEM-1", "issue" : "April", "issued" : { "date-parts" : [["2016"]] }, "page" : "16043", "title" : "Emerging flexible and wearable physical sensing platforms for healthcare and biomedical applications", "type" : "article-journal", "volume" : "2" }, "uris" : ["http://www.mendeley.com/documents/?uuid=e7e7753e-7c03-4ec6-89ca-de5e036dccac"] }], "mendeley" : { "formattedCitation" : "[3]", "plainTextFormattedCitation" : "[3]", "previouslyFormattedCitation" : "[3]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}. However, the integration of circuitry is a challenge due to the difficulty encountered directly depositing a conductive material. Frequently, cracks are formed in the photoresist during photolithography and in the metal during the sputtering processes. Moreover, adhesion is poor and additional adhesion layers, bonding agents and multi-steps (lift off and etching), are required to achieve a crack-free photoresist and metal patterning on PDMS {ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1002/adfm.200400189", "ISBN" : "1616-301X", "ISSN" : "1616301X", "abstract" : "This article describes the fabrication of durable metallic patterns that are embedded in poly(dimethylsiloxane) (PDMS) and demonstrates their use in several representative applications. The method involves the transfer and subsequent embedding of micrometer-scale gold (and other thin-film material) patterns into PDMS via adhesion chemistries mediated by silane coupling agents. We demonstrate the process as a suitable method for patterning stable functional metallization structures on PDMS, ones with limiting feature sizes less than 5\u2009\u03bcm, and their subsequent utilization as structures suitable for use in applications ranging from soft-lithographic patterning, non-planar electronics, and microfluidic (lab-on-a-chip, LOC) analytical systems. We demonstrate specifically that metal patterns embedded in both planar and spherically curved PDMS substrates can be used as compliant contact photomasks for conventional photolithographic processes. The non-planar photomask fabricated with this technique has the same surface shape as the substrate, and thus facilitates the registration of structures in multilevel devices. This quality was specifically tested in a model demonstration in which an array of one hundred metal oxide semiconductor field-effect transistor (MOSFET) devices was fabricated on a spherically curved Si single-crystalline lens. The most significant opportunities for the processes reported here, however, appear to reside in applications in analytical chemistry that exploit devices fabricated using the methods of soft lithography. Toward this end, we demonstrate durably bonded metal patterns on PDMS that are appropriate for use in microfluidic, microanalytical, and microelectromechanical systems. We describe a multilayer metal-electrode fabrication scheme (multilaminate metal\u2013insulator\u2013metal (MIM) structures that substantially enhance performance and stability) and use it to enable the construction of PDMS LOC devices using electrochemical detection. A polymer-based microelectrochemical analytical system, one incorporating an electrode array for cyclic voltammetry and a microfluidic system for the electrophoretic separation of dopamine and catechol with amperometric detection, is demonstrated.", "author" : [{ "dropping-particle" : "", "family" : "Lee", "given" : "Keon Jae", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Fosser", "given" : "Kari A.", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Nuzzo", "given" : "Ralph G.", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Advanced Functional Materials", "id" : "ITEM-1", "issue" : "4", "issued" : { "date-parts" : [[

"2005"]] }, "page" : "557-566", "title" : "Fabrication of stable metallic patterns embedded in poly (dimethylsiloxane) and model applications in non-planar electronic and lab-on-a-chip device patterning", "type" : "article-journal", "volume" : "15" }, "uris" : ["http://www.mendeley.com/documents/?uuid=67e0227f-09b0-471a-a29c-08bff3cb27ab"] }], "mendeley" : { "formattedCitation" : "[4]", "plainTextFormattedCitation" : "[4]", "previouslyFormattedCitation" : "[4]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}. Expensive vacuum techniques such as e-beam evaporation are used for metal deposition on PDMS-based substrates. Direct metal transfer technology is another example of metal deposition to polymer substrates. However, it requires an additional rigid substrate (e.g. glass and silicon wafer) to prepare metal patterns prior to their transfer to PDMS receiver substrate {ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1088/0960-1317/23/8/085016", "ISBN" : "0960-1317", "ISSN" : "09601317", "abstract" : "This paper describes the transfer of thin gold films deposited on rigid silicon substrates to polydimethylsiloxane (PDMS) with reliable and strong bonding. Modification of the Au surfaces with (3-mercaptopropyl) trimethoxysilane (MPTMS) as a molecular adhesive was carried out to promote adhesion between Au and PDMS. The degree of bonding with respect to the concentration of MPTMS, treatment time and methods of deposition was investigated by a simple adhesion test using two different adhesive tapes. The effect of hydrolysis of MPTMS is discussed based on the bonding mechanism of MPTMS to the PDMS prepolymer. Also, the adsorption of MPTMS on Au deposited by different methods is discussed. The results indicate that liquid deposition of MPTMS provides the strongest adhesion between Au and PDMS among the different deposition methods and the different linker molecules. Based on these studies, the Au patterns with linewidth of less 2 mu m were successfully transferred to PDMS with reliable and strong bonding in a full 3 inch wafer scale, using a dry peel-off process.", "author" : [{ "dropping-particle" : "", "family" : "Byun", "given" : "Ikjoo", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Coleman", "given" : "Anthony W.", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Kim", "given" : "Beomjoon", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Journal of Micromechanics and Microengineering", "id" : "ITEM-1", "issue" : "8", "issued" : { "date-parts" : [["2013"]] }, "title" : "Transfer of thin Au films to polydimethylsiloxane (PDMS) with reliable bonding using (3-mercaptopropyl)trimethoxysilane (MPTMS) as a molecular adhesive", "type" : "article-journal", "volume" : "23" }, "uris" : ["http://www.mendeley.com/documents/?uuid=c4d673b0-36e4-4467-a06a-6bdc8d2de86a"] }], "mendeley" : { "formattedCitation" : "[5]", "plainTextFormattedCitation" : "[5]", "previouslyFormattedCitation" : "[5]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}. Therefore, it is important to develop an economic and simple technique, which provides a high metal-to-PDMS surface adhesion and which remains conductive whilst it undergoes bending and stretching deformations. The formation of conductive features by direct metallization triggered by light patterning addresses these issues {ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1002/adfm.201870041", "abstract" : "In article number 1704451, Jose Marques-Hueso and coworkers present a rapid photopatterning method that allows for selective plating of 2D and 3D microcircuity on polyetherimide. Conductive copper tracks as small as 18 \u03bcm are accessible by local light-induced synthesis of silver nanoparticles on the substrate. Applicability of the method for flexible polytherimide films and 3D-printed substrates shows promise for electronics manufacturing.", "author" : [{ "dropping-particle" : "", "family" : "Marques\u2010Hueso J., Thomas D. A. Jones, David E. Watson, Assel Ryspayeva, Mohammadreza Nekouie Esfahani , Matthew P. Shuttleworth, Russell A. Harris, Robert W. Kay", "given" : "Marc P. Y. Desmulliez", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Advanced Functional Materials", "id" : "ITEM-1", "issue" : "6", "issued" : { "date-parts" : [["2018"]] }, "page" : "2018", "title" : "Flexible Electronics: A Rapid Photopatterning Method for Selective Plating of 2D and 3D Microcircuitry on Polyetherimide (Adv. Funct. Mater. 6/2018)", "type" : "article-journal", "volume" : "28" }, "uris" : ["http://www.mendeley.com/documents/?uuid=22ee8ce4-4a29-459c-957f-48fdbbec09b5"] }], "mendeley" : { "formattedCitation" : "[6]", "plainTextFormattedCitation" : "[6]", "previouslyFormattedCitation" : "[6]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}.

In this work, we have developed a rapid technique for the direct metallization of PDMS substrates by reliable photolithography and electroless copper plating methods. Fig. 1 shows the newly developed photo-patterning and metallization steps. Modified DNQ-novolac photoresist polymer (hereafter - polymer) was mixed with $AgClO_4$ salt, which was thermally reduced to Ag nanoparticles (NPs) inside the polymer during a hard bake step [4]. Crack-free metal patterns are achieved through optimization of photolithography parameters. Analysis of cracking and buckling formations in polymer and metal films, under-optimized and non-optimized fabrication parameters is performed, through the study of optical micrographs. The electromechanical behaviour of metal patterns on PDMS is investigated by measuring changes in electrical conductivity in response to strain and bending cycling deformations, As a proof of concept, we demonstrate a flexible light emitting diode (LED) circuit fabricated by the developed metallization method and show the circuit working during the bending test.

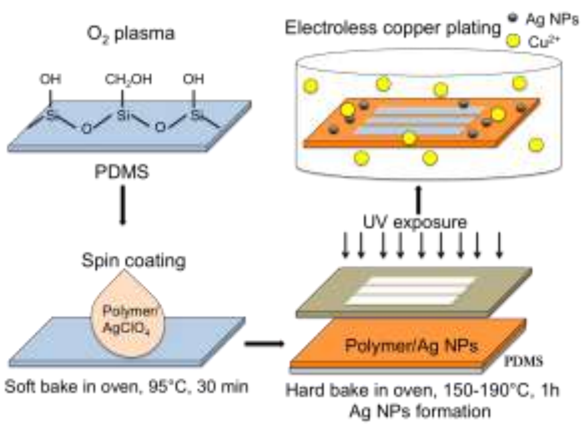


Fig 1. The schematic steps of the direct metallization of PDMS substrate using photolithography and electroless copper plating.

2. Experimental

Two types of PDMS were tested: commercial PDMS-based gel sheets supplied by Gel-Pak® (150 μm thickness), and handmade PDMS substrates prepared by curing a silicone elastomer with a curing agent in a 10:1 ratio. PDMS substrates were treated with oxygen plasma prior to polymer/$AgClO_4$ spin coating to increase PDMS surface roughness. Oxygen plasma was applied by PLASMALAB (Oxford Instruments Plasma Technology**)** for 10 s at 100 mbar pressure.

2.1 Synthesis of Ag NPs seeds inside the polymer and photo-patterning method

0.1 M silver perchlorate ($AgClO_4$, Sigma Aldrich, 97 %) concentration was received by dissolving it in 1-methoxy 2-propylacetate (MPA) (Sigma Aldrich, 99%). Ma-P 1215 photoresist (Microresist Technology) was mixed with silver solution in 1:1 ratio. The resultant mixture was spin coated on PDMS substrates at 3000 rpm for 30 s and soft baked at 95°C for 30 minutes in an oven. PDMS substrates were exposed to UV light at 14 mWcm^{-2} with Karl Suss MJB 3 UV mask aligner and developed with AZ 326 developer. The samples were hard baked at 150-190°C for 1 hour in oven at a ramping temperature.

2.2 Fabrication of electroless copper films and interconnections

Electroless copper bath solution was prepared by dissolving 6 g of copper sulfate (98 %, Sigma Aldrich), 8 g of sodium hydroxide (98.5 %, Acros Organics), and 28 g of potassium tartrate (99 %, Fisher Scientific) into 200 ml of DI water. Before the electroless plating, the concentrated solution was diluted with DI water in the ratio of 1:1 and 2 ml of formaldehyde (37 %, Acros Organics) was added. Ma-P 1200 series photoresists have an outstanding stability in acid and alkaline plating baths, therefore, treated substrates were immersed into electroless copper bath for 10 minutes. Electroless copper plating was conducted at 30°C.

Flexible LED circuit was fabricated as a proof of concept. Conductive electroless copper interconnections were fabricated on 1 mm thick PDMS, using a homemade photo-mask and its bending properties were tested. Flexible LED circuit consists of a 3 mm LED with a 3 V battery that were connected to the flexible interconnections.

2.3 Characterization and measurement

Copper film thickness and PDMS surface roughness were measured by Dektak^{3} Stylus optical profilometer and optical images of the film surface were obtained using LEICA CTR 6500 instrument.

All resistance measurements were performed by two-point probe technique using SIGNATONE S-1160 probe station. The metal plating quality was tested with IPC -TM-650 scotch tape test **{**ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "container-title" : "Association Connecting Electronics Industries", "id" : "ITEM-1", "issued" : { "date-parts" : [["2004"]] }, "number-of-pages" : "2-5", "publisher-place" : "2215 Sanders Road Northbrook, IL 60062-6135", "title" : "Ipc-tm-650 test methods manual 1", "type" : "report" }, "uris" : ["http://www.mendeley.com/documents/?uuid=52b42335-02ce-401b-9d96-8d2b6b6373fa"] }], "mendeley" : { "formattedCitation" : "[7]", "plainTextFormattedCitation" : "[7]", "previouslyFormattedCitation" : "[7]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }**}**. Pressure sensitive tape Type 1, Class B was firmly applied to metal surface removing all air entrapment. The test was performed three times with fresh tape used for each test. The tapes were visually examined for presence of any portion of the film having been removed from the PDMS surface.

The strain was applied to metallized PDMS substrates with the handmade mechanical strain machine that consists of a displacement-sliding table and clamps to hold a film. Mechanical strain machine is capable to apply up to 80% uniaxial strain to metallized patterns. The bending cycles experiments were conducted on a Dynamic Mechanical Analyzer (DMA, TA Instruments, Model Q800) in single cantilever mode with amplitudes of 2.5 mm and 5.0 mm at a frequency of 1Hz at room temperature. Tested PDMS substrates with copper film have 17.1 mm length, 10.4 mm width and 1.2 mm thickness.

3. Results and discussion

The surface roughness of PDMS-based Gel-Pak® films increased from 10 ± 2 nm to 53 ± 4 nm after oxygen plasma treatment. As for handmade PDMS, the surface roughness increased from 7 ± 2 nm to 33 ± 8 nm. The increase of the surface roughness allowed uniform coating of the PDMS surface with polymer/$AgClO_4$ solution. The formation and growth of Ag NPs inside the polymer matrix is occurred by thermal induced reduction of Ag(I) to Ag(0) at high temperatures {ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1039/c0jm01226b", "ISSN" : "0959-9428", "abstract" : "In this work we report on a method to synthesize Ag-Au patterns by UV lithography. The photoresists are based on DNQ-novolac as the polymer matrix, and Ag(I) and Au(III) salts as the nanoparticle precursors. After UV lithography, silver and gold nanoparticles are in situ synthesized inside the polymer patterns during a post bake. The resulting structured nanocomposite shows a characteristic absorbance spectrum related to the plasmon frequency of the synthesized noble metal NPs. This method represents a fast, simple and low-cost approach to the formation of extended polymer patterns with embedded silver or gold NPs. Moreover, it is a mechanism to position nanometric particles with micrometric resolution, which represents a useful tool for nanoscience. Furthermore, even with the polymeric cover, NPs plasmon resonance is affected by the binding of some organic molecules. This concept has been proven with 2-mercaptoethanol molecules, which demonstrates the feasibility of localized surface plasmon resonance chemo/biosensors by using the proposed technology.", "author" : [{ "dropping-particle" : "", "family" : "Marqu\u00e9s-Hueso", "given" : "Jos\u00e9", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Abargues", "given" : "Rafael", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Vald\u00e9s", "given" : "Jos\u00e9 L.", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Mart\u00ednez-Pastor", "given" : "Juan P.", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Journal of Materials Chemistry", "id" : "ITEM-1", "issue" : "35", "issued" : { "date-parts" : [["2010"]] }, "page" : "7436", "title" : "Ag and Au/DNQ-novolac nanocomposites patternable by ultraviolet lithography: a fast route to plasmonic sensor microfabrication", "type" : "article-journal", "volume" : "20" }, "uris" : ["http://www.mendeley.com/documents/?uuid=37e407e9-79fb-4c4e-b3e2-c2a5fa52d8e6"] }], "mendeley" : { "formattedCitation" : "[8]", "plainTextFormattedCitation" : "[8]", "previouslyFormattedCitation" : "[8]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}. The Ag NPs act as seeding catalysts for copper ions adsorption during the electroless copper metallization step { ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "author" : [{ "dropping-particle" : "", "family" : "Marques-Hueso", "given" : "Jose", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Morton", "given" : "Jonathan", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Wang", "given" : "Xiangfu", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Bertran Serra", "given" : "Enric", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Desmulliez", "given" : "Marc", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Nanotechnology", "id" : "ITEM-1", "issued" : { "date-parts" : [["2018"]] }, "title" : "Photolithographic nanoseeding method for selective synthesis of metal-catalysed nanostructures", "type" : "article-journal" }, "uris" : ["http://www.mendeley.com/documents/?uuid=7f57c50f-4022-4e3f-9406-5828bb473b3c"] }], "mendeley" : { "formattedCitation" : "[9]", "plainTextFormattedCitation" : "[9]", "previouslyFormattedCitation" : "[9]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}. Electroless copper plating for 10 minutes resulted in copper thickness of 0.44 ± 0.05 μm, however, deposition of the metal film over the elastomeric surface may result in the formation of cracks and buckles. For this reason, we discuss in the following sections film morphology and study electromechanical behaviour of the copper film on PDMS surface by applying strain and bending deformations.

3.1 Morphology analysis of polymer/AgNPS and metal film on PDMS

Process-induced cracks in spin coated polymer/$AgClO_4$ film on PDMS may occur during the lithographic patterning processes such as soft and hard baking steps. These cracks arise from the expansion of the elastomer surface due to applied temperatures, which induces a thermal tensile stress over the polymer/$AgClO_4$ film. This may lead to the polymer/$AgClO_4$ film rupturing and furthermore, it may also cause the underlying PDMS substrate to fracture { ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1088/0022-3727/47/10/105401", "ISBN" : "0022-3727", "ISSN" : "00223727", "abstract" : "Flexible electronics and other polymer-based devices demand effective metallization of thin metal films over soft substrates. However, metallization of thin films over soft elastomers such as polydimethylsiloxane (PDMS) often leads to crack formation and morphological changes in the film as well as over the elastomeric surface offering limited applications in the development of biomedical microdevices. In the present study, optimized sputtering conditions like variations in base vacuum, working pressure, sputtering power and time required for crack-free uniform deposition of nichrome thin film over a PDMS surface are discussed. Analysis of film buckling and cracking under optimized and non-optimized conditions is performed through study of plasma colour, optical microphotographs and scanning electron microscopy images. The Young's modulus of an oxidized PDMS surface under no-crack conditions is estimated through the buckling mechanics of thin films and is found to vary with deposition conditions. The present investigation establishes that interaction of a PDMS surface with plasma modifies the surface properties to the extent that its mechanical properties either become compliant to the overlying deposited film, forming buckles, or become noncompliant, leading to cracked films. Fabrication of microheaters on crack-free nichrome thin film under optimized conditions was carried out to explore its suitability in flexible electronics.", "author" : [{ "dropping-particle" : "", "family" : "Maji", "given" : "Debashis", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Das", "given" : "Soumen", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Journal of Physics D: Applied Physics", "id" : "ITEM-1", "issue" : "10", "issued" : { "date-parts" : [["2014"]] }, "title" : "Analysis of plasma-induced morphological changes in sputtered thin films over compliant elastomer", "type" : "article-journal", "volume" : "47" }, "uris" : ["http://www.mendeley.com/documents/?uuid=f29b1dda-642e-4cd0-81cd-21c6c04651c4"] }], "mendeley" : { "formattedCitation" : "[10]", "plainTextFormattedCitation" : "[10]", "previouslyFormattedCitation" : "[10]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }**}**. Fig. 2a shows the process induced cracks in PDMS when films experience sudden temperature change due to heating and cooling. Developed fractures in PDMS during the soft and hard baking steps further effect the quality of metal patterns on the PDMS surface (Fig. 2b) therefore, the careful control of baking temperature should be performed. Cracks were eliminated during soft and hard baking processes by utilizing homogenous heating and cooling in an oven by applying temperature ramping.

Compressive stress may also build up during the cooling process which may result in buckling or wrinkle formations **{**ADDIN CSL_CITATION { "citationItems" : [{ "id" : "ITEM-1", "itemData" : { "DOI" : "10.1088/0022-3727/47/10/105401", "ISBN" : "0022-3727", "ISSN" : "00223727", "abstract" : "Flexible electronics and other polymer-based devices demand effective metallization of thin metal films over soft substrates. However, metallization of thin films over soft elastomers such as polydimethylsiloxane (PDMS) often leads to crack formation and morphological changes in the film as well as over the elastomeric surface offering limited applications in the development of biomedical microdevices. In the present study, optimized sputtering conditions like variations in base vacuum, working pressure, sputtering power and time required for crack-free uniform deposition of nichrome thin film over a PDMS surface are discussed. Analysis of film buckling and cracking under optimized and non-optimized conditions is performed through study of plasma colour, optical microphotographs and scanning electron microscopy images. The Young's modulus of an oxidized PDMS surface under no-crack conditions is estimated through the buckling mechanics of thin films and is found to vary with deposition conditions. The present investigation establishes that interaction of a PDMS surface with plasma modifies the surface properties to the extent that its mechanical properties either become compliant to the overlying deposited film, forming buckles, or become noncompliant, leading to cracked films. Fabrication of microheaters on crack-free nichrome thin film under optimized conditions was carried out to explore its suitability in flexible electronics.", "author" : [{ "dropping-particle" : "", "family" : "Maji", "given" : "Debashis", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }, { "dropping-particle" : "", "family" : "Das", "given" : "Soumen", "non-dropping-particle" : "", "parse-names" : false, "suffix" : "" }], "container-title" : "Journal of Physics D: Applied Physics", "id" : "ITEM-1", "issue" : "10", "issued" : { "date-parts" : [["2014"]] }, "title" : "Analysis of plasma-induced morphological changes in sputtered thin films over compliant elastomer", "type" : "article-journal", "volume" : "47" }, "uris" : ["http://www.mendeley.com/documents/?uuid=f29b1dda-642e-4cd0-81cd-21c6c04651c4"] }], "mendeley" : { "formattedCitation" : "[10]", "plainTextFormattedCitation" : "[10]", "previouslyFormattedCitation" : "[10]" }, "properties" : { }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }}. The temperature chosen during hard baking step is to promote thermal reduction of Ag(I) to Ag NPs. At 190°C, buckles were developed (Fig. 2 c-d), however, decreasing the temperature down to 150°C reduced buckling formation. Fig. 3 shows received crack-free polymer/Ag NPs patterns which lead to crack-free copper metal patterns on PDMS surface.

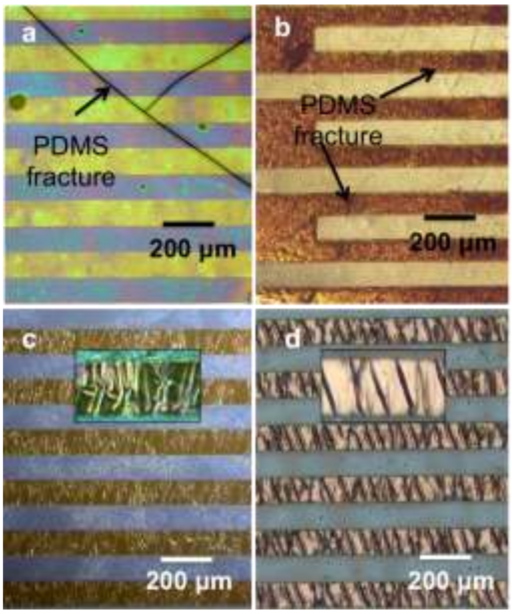


Fig. 2. Study of optical micrographs for PDMS fractures due to sudden baking temperature changes (a) polymer/Ag NPs patterns and (b) copper metal patterns. Buckle formations due to 190°C hard baking temperature (c) polymer/Ag NPs patterns and (d) copper metal patterns.

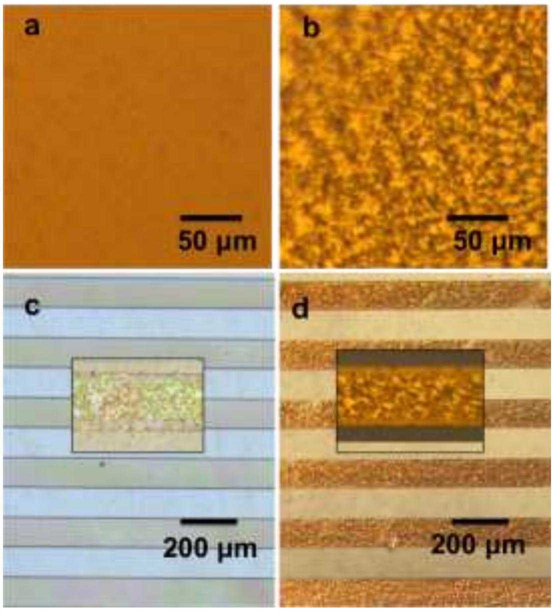


Fig. 3. Study of optical micrographs: (a) polymer/Ag NPs film baked at 150°C, (b) copper metal film, (c) polymer/Ag NPs pattern baked at 150°C, (d) copper metal pattern.

3.2 Mechanical and Electrical properties

The formation of strong adhesion between the copper layer and PDMS is important for mechanical and electrical stability. The fabricated copper film on PDMS substrate has a strong adhesion and passes the scotch-tape tests. The mechanical properties of copper micropatterns on PDMS substrate is further tested with application of the uniaxial longitudinal strain parallel to the direction of the copper micro-lines. Fig. 4 shows a development of strain-induced cracking in copper patterns on PDMS substrate as a function of the applied uniaxial strain. At zero strain, no process-induced cracks are observed. The strain-induced cracks start to form at 10% applied strain. As the applied strain increases, the density of cracks increases (Fig. 4g). It is also observed that the increase of the applied strain results in an enlarged crack width. The arrows in Fig. 4 (d-e) show the visual comparison between the crack widths due to the increase of the consecutive applied strain.

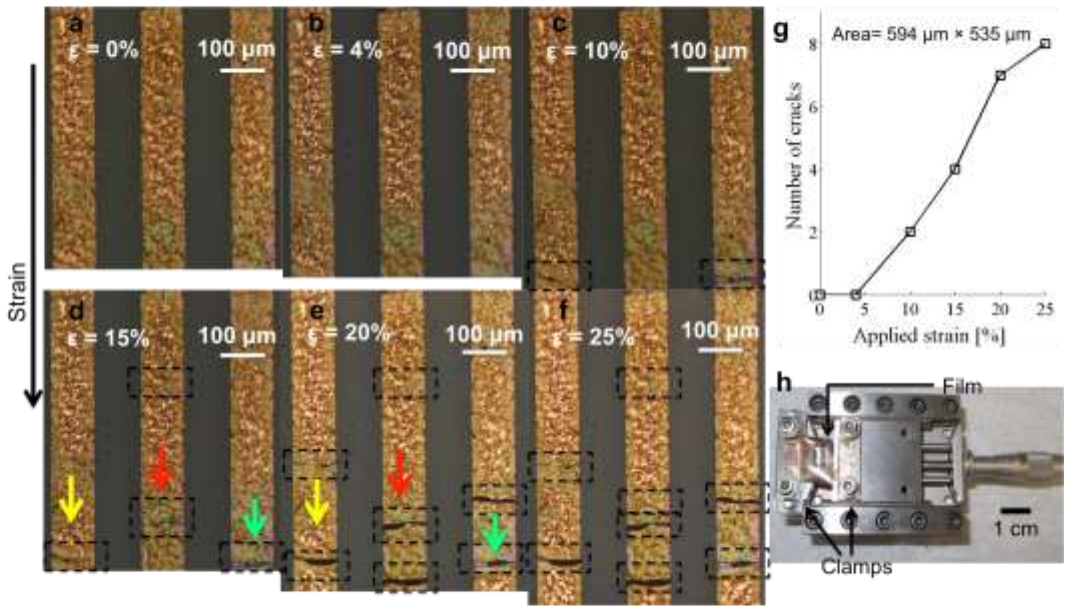


Fig. 4. Development of the strain-induced cracks in copper micropattern due to applied uniaxial strain. Strain is applied parallel to the copper line patterns. From (a) to (f) the applied strain varies from 0% to 25%. (g) Density of strain-induced cracks as a function of the applied strain. (h) handmade mechanical strain machine.

Fig. 5a shows the electromechanical behaviour of the copper film as a function of the applied strain. At zero strain, conductivity of the copper film is $(3.6 \pm 0.7) \times 10^7$ S/m. The conductivity drops to $(2.5 \pm 1.3) \times 10^7$ S/m at 10% strain. The longitudinal applied strain leads to the formation of horizontal micro-cracks in the copper film. Therefore, formed micro-cracks contribute to a reduction in the electrical conductivity. Further increase in the strain leads to a more discontinuous copper film with a conductivity approaching $(0.5 \pm 0.5) \times 10^7$ S/m at 15% applied strain. To further study the electromechanical behaviour of the copper film on the PDMS substrate, mechanical cycling tests were performed. Fig. 5b shows a change in normalized resistance (R/R_0) as a function of the bending cycles. Copper films were bended to 2.5 and 5.0 mm amplitudes. The resistance increased by almost 1.4 times when copper film was bended for 1000 cycles for both bending amplitudes. As the bending proceeded, the change in resistance increased and the conductivity dropped by a factor of two when copper film was bended to 2.5 mm amplitude and a factor of 4.5 when copper film was bended to 5.0 mm amplitude, after 10 000 cycles.

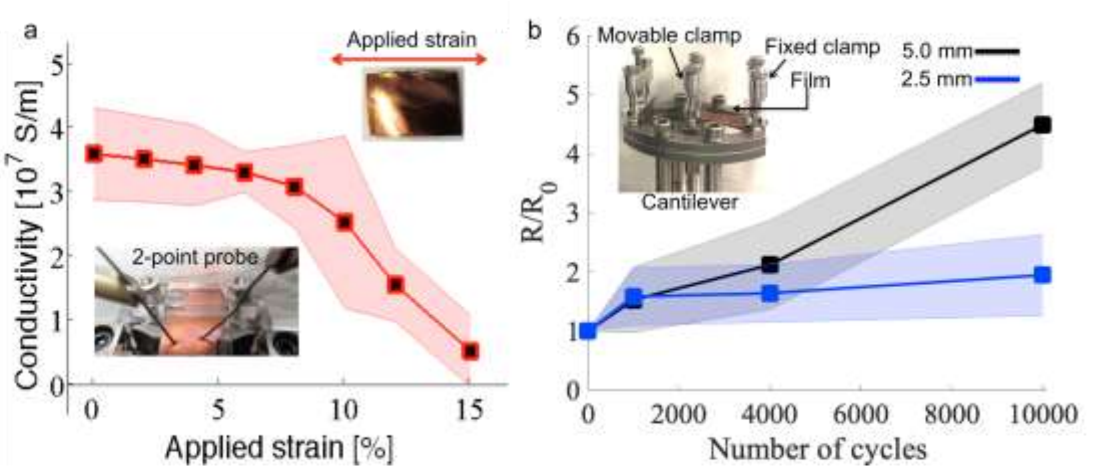


Fig.5. Dynamic electromechanical analysis of the copper-plated PDMS films. (a) Change in conductivity as a function of the applied strain. The insets show a copper film with the direction of the applied strain and a set up for resistance measurement with two-point probe. (b) Change in resistance during 10 000 cycling test for 2.5 mm and 5 mm amplitudes. The inset shows a cantilever with the movable and fixed clamps with a clamped film.

3.3 Application. Interconnections and flexible electronic circuit

Copper-plated PDMS was tested as a flexible LED circuit. Fig. 6a shows electroless copper interconnections fabricated on 1 mm thick PDMS substrate. An LED and battery were attached to the interconnections to form an electronic circuit (Fig.6b). With the battery on, we observed the LED to light up. A static bending test was further performed to study the electrical properties of the electroless copper interconnects on the PDMS surface (Fig.6 c-f). LED functioning was observed while the circuit was bent to 45°, 90°, 135° and 180°. During the static bending, interconnections remained conductive and LED remained switched on up to 180° bending angle.

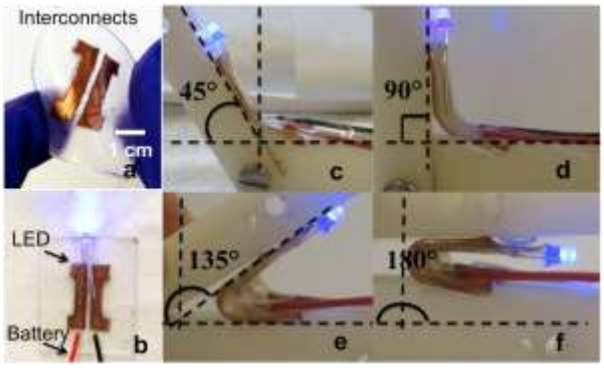


Fig. 6. Application of the PDMS metallized with copper composite. (a) Interconnections, (b) LED electronic circuit, (c-f) static bending tests of the flexible LED circuit.

4. Conclusions

We have developed a direct, selective and rapid metallization method of PDMS elastomers. Formed copper films and micro-patterns have advantages of high conductivity and good adhesion to PDMS substrate. Optimization of photolithographic parameters reduced process-induced cracks and buckles in polymer/$AgClO_4$ and subsequently in copper layer. The applied uniaxial strain resulted in crack-free copper film up to 10% strain. The conductivity shows good stability up to 10% applied strain, after which conductivity dropped 1.4 times compared to the initial measurement. Flexible LED circuit demonstrated that copper-plated PDMS has a high flexibility (up to 180°). The proposed low-cost and rapid metallization method of PDMS substrates is a promising fabrication technique for use in flexible and stretchable electronics applications.

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